

An ab initio and DFT study on the hydrolysis of carbonyl dichloride

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Abstract

Hydrolysis of carbonyl dichloride or phosgene (Cl_2CO) in gas phase has been investigated at Hartree–Fock, density functional and ab initio levels of theory. The effects of basis sets on the energetics of the reaction have also been explored. Calculations reveal that initially carbonyl dichloride and water form a weak complex and this complex can react further in two ways. In Path 1, water adds on to carbonyl dichloride across carbonyl bond in a concerted fashion to give dichloromethane diol, and this diol decomposes to form chloro formic acid by *syn*-1,2-elimination of HCl and forms CO_2 and HCl as final products. Path 2 is the concerted addition of water across carbon chlorine bond and elimination of HCl in a single step leading to the formation of chloro formic acid directly. This second path that skips the formation of dichloromethane diol is observed to be very low lying and hence is kinetically favored. Addition of second water molecule to the reacting system is found to catalyze the reaction by stabilizing the complex, intermediate and transition states and reduces the activation energy to $24.6 \text{ kcal mol}^{-1}$ compared to $29.9 \text{ kcal mol}^{-1}$ for a single water molecule.

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1. Introduction

Carbonyl dichloride or phosgene (Cl_2CO) is a biologically harmful but industrially important gas with an annual production of two million tons. This gas is often used in the synthesis of isocyanates, polyurethane, polycarbonate resins, carbamates, organic carbonates, pesticides, herbicides, dyes, pharmaceuticals, and in metallurgy. Carbonyl dichloride is produced in the stratospheric region of the atmosphere [1,2] through the photolysis of CFC's by UV-radiation and the atmospheric chemistry of carbonyl dichloride has gained importance in view of its environmental significance [3]. It is known that carbonyl dichloride gets incorporated into rain and fog water and undergo hydrolysis in aqueous solution to form carbon dioxide and hydrochloric acid. The mechanism of this reaction still remains elusive even though a significant amount of work has been done on the hydrolysis of carbonyl dichloride [4–6]. Although the mechanism of hydrolysis of

its congeners H_2CO [7], F_2CO [8,9], and Br_2CO [10] in the gas phase has been reported, there are no theoretical studies devoted to the mechanism of hydrolysis of Cl_2CO apart from the formation of phosgene–water weak complex [6]. Therefore in this paper, we have modeled the hydrolysis of Cl_2CO in gas phase at Hartree–Fock, density functional and ab initio levels of theory and report the mechanism. Catalysis of the reaction by water molecules has also been investigated by explicit addition of second water molecule to the reacting species. The effect of different basis sets on the energetics of the reaction has been examined at density functional level of theory. Mechanism of this reaction is compared with that of hydrolysis of Br_2CO and of F_2CO .

2. Computational details

Density functional theory and ab initio calculations have been performed using GAUSSIAN 98 [11]. Optimizations have been performed at HF, MP2, and B3LYP levels. MP4 single point energy calculation has been performed on MP2 geometries. The calculations have also been performed at DFT level using different basis sets viz. 6-31G(d),

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6-311G(d), 6-31+G(d), 6-31G(d,p), 6-311++G(d,p) [12, 13]. In DFT calculations, Becke's three-parameter non-local exchange functional with the non-local correlation functional of Lee, Yang, and Parr has been used [14]. All equilibrium geometries have been fully optimized to better than 0.001 Å for a bond distance and 0.1° for bond angles. Stationary points have been located and characterized by computing the vibrational frequencies for reactants, intermediates, products, and transition states. The reactants, intermediates and products have all frequencies real and the transition states had single imaginary frequency. Transition states have been further confirmed by examining their transition vectors and by animating the imaginary frequency using a visualization program MOLEKEL [15]. Catalysis by water molecule has been studied by explicit inclusion of a second water molecule to the reacting system at B3LYP/6-311++G(d,p).

3. Results and discussion

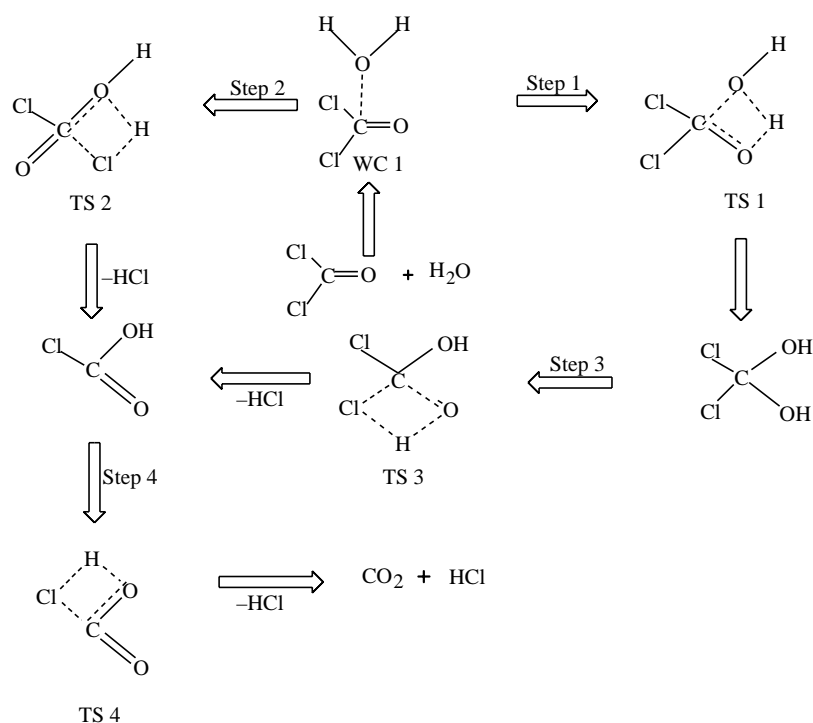
The detailed mechanistic scheme of the hydrolysis of carbonyl dichloride is presented in Schemes 1 and 2. Fig. 1 shows the energy profiles of the reaction in gas phase, Figs. 2 and 3 give geometries of transition state species and weak complexes. The activation and reaction energies for the reaction computed at various levels in gas phase are collected in Table 1. Table 2 presents B3LYP/6-311++G(d,p) activation and reaction energies for the gas phase hydrolysis of carbonyl difluoride, carbonyl dichloride and carbonyl

dibromide and Table 3 lists activation and reaction energies computed at B3LYP level with different basis sets.

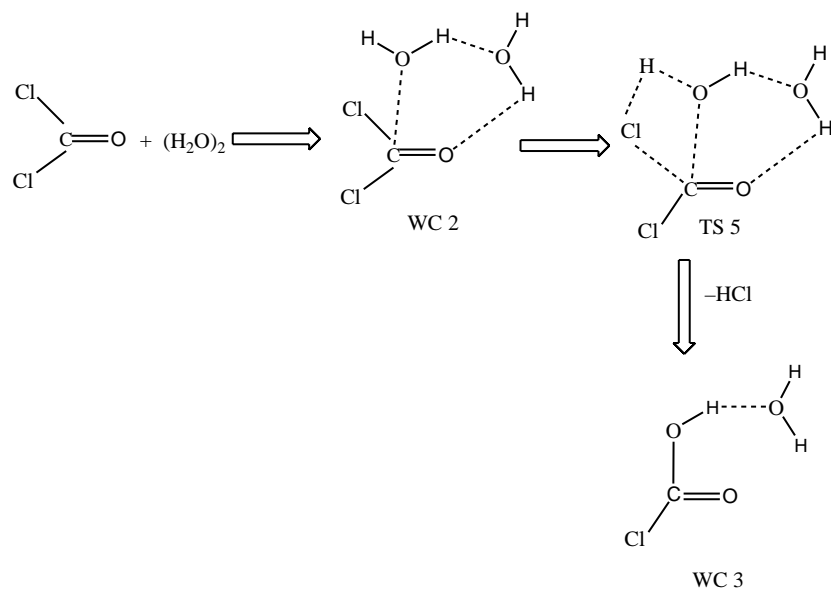
Water can add concertedly to carbonyl dichloride in two ways: (i) across the C=O bond (Path 1); (ii) across the C–Cl bond (Path 2) as denoted in Scheme 1. Path 1 describes the formation of dichloromethane diol as an intermediate on the addition of water to carbonyl dichloride. This diol can further react eliminating one molecule of HCl molecule by *syn*-1,2-elimination forming chloro formic acid as a second intermediate. Subsequently, chloro formic acid eliminates one molecule of HCl to form CO₂. The above reactions are depicted as steps 1, 3, and 4 in Scheme 1 and they constitute Path 1. Path 2 is the addition of water across the carbon chlorine bond of carbonyl dichloride and eliminating HCl simultaneously to give chloro formic acid and this in the second step decomposes to CO₂ and HCl. Steps 2 and 4 in Scheme 1 constitute Path 2. Thus there are two possible mechanisms for this reaction and they differ only in the manner in which how the chloro formic acid is formed. Decomposition of chloro formic acid to CO₂ and HCl is common to both Path 1 and 2.

3.1. Energetics

Hydrolysis of Cl₂CO in gas phase is a multi-step reaction in which Cl₂CO initially forms a weak complex (WC1) with one molecule of water. Activation energy values with respect to reactants obtained at various levels (Table 1) and the energy profiles (Fig. 1) show that the initial step in both paths, step 1 of Path 1 and step 2 of Path 2 in Scheme 1, is



Scheme 1. Detailed scheme for the gas phase hydrolysis of carbonyl dichloride.



Scheme 2. Scheme for the hydrolysis of carbonyl dichloride with second water molecule catalyzing the reaction.

rate determining and step 1 involves high activation energy compared to step 2. This clearly demonstrates that direct formation of ClCOOH is favored. ClCOOH formed in step 2 is chemically activated and decomposes in the subsequent step into CO_2 and HCl. Therefore, the mechanism of this

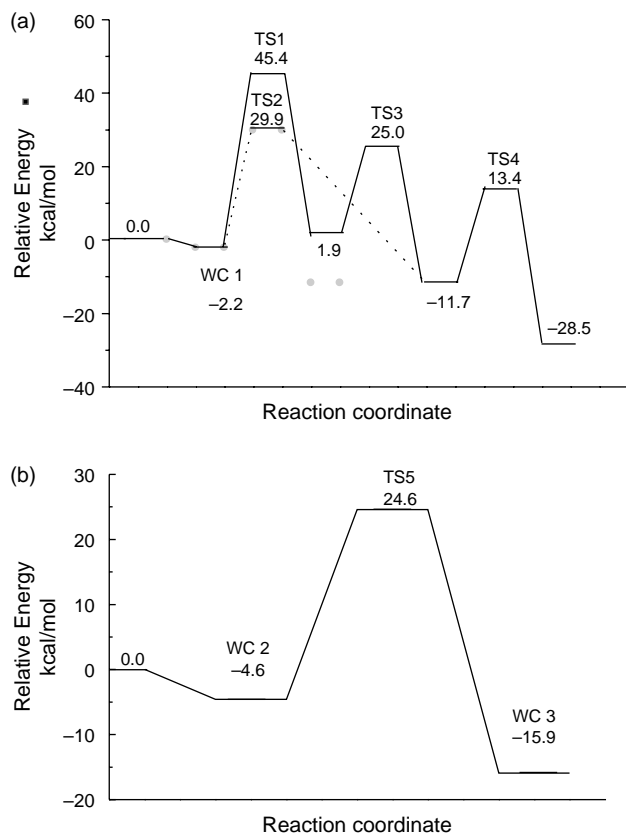


Fig. 1. Energy profile for the hydrolysis of carbonyl dichloride in gas phase at B3LYP/6-311++G(d,p) level (a) $\text{Cl}_2\text{CO} + \text{H}_2\text{O}$ (b) $\text{Cl}_2\text{CO} + 2\text{H}_2\text{O}$.

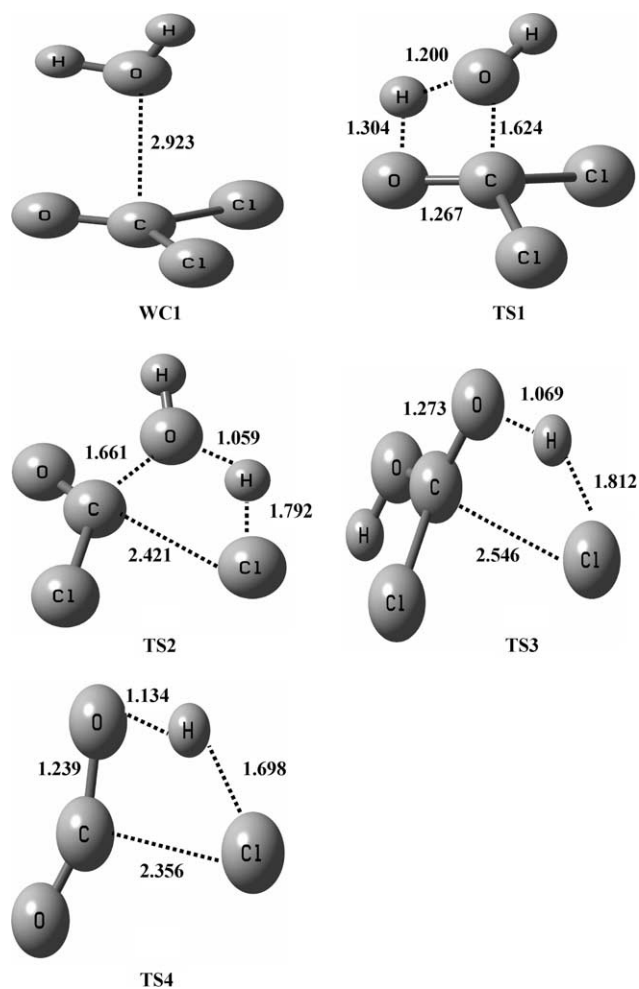


Fig. 2. B3LYP/6-311++G(d,p) geometries of the weak complex and transition state species for the reaction of hydrolysis of carbonyl dichloride in gas phase.

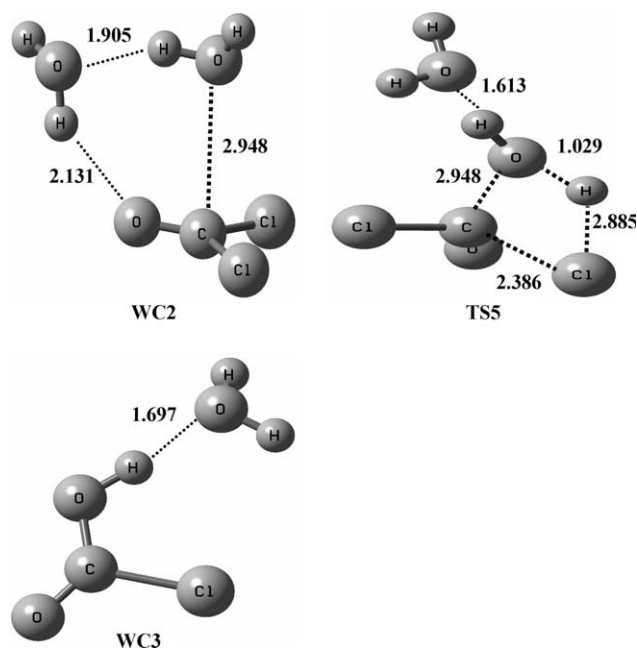


Fig. 3. B3LYP/6-311++G(d,p) geometries of the weak complex and transition state species for the reaction of Cl_2CO in gas phase with two water molecules.

reaction is Path 2 and the rate determining process is step 2. Computed activation energies at various levels (Table 1) also confirm this. It is worthwhile comparing the activation energy obtained at various levels with the experimental value reported by Butler and Snelson [5]. These authors have performed the hydrolysis of Cl_2CO and a set of halogenated acetyl chloride in gas phase in the temperature range of 533–619 K and have reported $14.2 \pm 2.1 \text{ kcal mol}^{-1}$ as activation energy for the hydrolysis of Cl_2CO . The authors have mentioned that the data points showed lot of scatter in the Arrhenius plot. Therefore, these results have to be

treated with caution while comparing them with calculated results. Among HF, DFT, MP2, and MP4 activation energies, the DFT value is the closest to the experimental value. The discrepancy between the DFT activation energy, $29.9 \text{ kcal mol}^{-1}$, and the experimental activation energy reported by Butler and Snelson, $14.2 \pm 2.1 \text{ kcal mol}^{-1}$, can be explained considering two factors: (i) possible proton tunneling; and (ii) by active participation of second water in catalyzing the reaction. We discuss the second aspect separately in a later section and discuss here the possibility of tunneling on the reaction rates. All the transition states of this reaction involve movement of proton in the TS, and there is a possibility that proton tunneling might occur to reduce the barrier height. The transition states involved in the reaction have the frequency values of 1254.81i, 497.17i, 1801.88i, and 844.21i for TS1, TS2, TS3, and TS4, respectively, and these high values are due to the involvement of heavy atoms such as chlorine in the reaction coordinate. All the above frequency values are below the cut-off value of 2000i suggested by Wigner [16] for the tunneling and this suggests that the possibility of tunneling can be ruled out.

3.2. Comparison of the hydrolysis of F_2CO , Cl_2CO , and Br_2CO

If the energy profiles for Paths 1 and 2 of the Cl_2CO with water are compared with those reported for the reaction of Br_2CO [10] and F_2CO [9], the following points emerge. Both Francisco and Zachariah and co-workers have discussed the possibility of these two competing steps for the hydrolysis of Br_2CO and F_2CO . Zachariah and co-workers find the direct formation of FCOOH more favorable and this involves a low barrier compared to the alternative path by $4.6 \text{ kcal mol}^{-1}$. Francisco reports a barrier for

Table 1
Activation and reaction energies (kcal mol^{-1}) of the $\text{Cl}_2\text{CO} + \text{H}_2\text{O}$ reaction in gas phase computed at various levels

| Reaction | HF | | B3LYP | | MP2 | | MP4 | |
|--|-------|--------|-------|--------|-------|--------|-------|--------|
| | E_a | E_r | E_a | E_r | E_a | E_r | E_a | E_r |
| $\text{Cl}_2\text{CO} + \text{H}_2\text{O} \rightarrow \text{Cl}_2(\text{OH})_2$ | 59.55 | -0.77 | 45.41 | 1.87 | 44.48 | 0.95 | 45.24 | 1.86 |
| $\text{Cl}_2\text{CO} + \text{H}_2\text{O} \rightarrow \text{ClCOOH} + \text{HCl}$ | 41.63 | -17.45 | 29.88 | -11.71 | 34.30 | -9.46 | 34.20 | -9.68 |
| $\text{Cl}_2\text{C}(\text{OH})_2 \rightarrow \text{ClCOOH} + \text{HCl}$ | 27.75 | -16.67 | 22.68 | -13.59 | 30.32 | -10.42 | 29.43 | -11.55 |
| $\text{ClCOOH} \rightarrow \text{CO}_2 + \text{HCl}$ | 34.51 | -22.06 | 25.13 | -16.77 | 28.09 | 17.76 | 27.83 | -18.39 |

Table 2
Activation and reaction energies (kcal mol^{-1}) of $\text{X}_2\text{CO} + \text{H}_2\text{O}$ reaction in gas phase at B3LYP/6-311++G(d,p)

| Reaction | X=F | | X=Cl | | X=Br | |
|---|---------------|-----------------|-------|--------|--------------|----------------|
| | E_a | E_r | E_a | E_r | E_a | E_r |
| $\text{X}_2\text{CO} + \text{H}_2\text{O} \rightarrow \text{XCOOH} + \text{HX}$ | 37.11 (29.11) | -9.86 (-11.3) | 29.88 | -11.71 | 30.22 (31.8) | -9.78 (-8.8) |
| $\text{XCOOH} \rightarrow \text{HX} + \text{CO}_2$ | 32.82 (35.23) | -12.76 (-12.09) | 25.13 | -16.77 | 22.75 (21.8) | -16.31 (-20.3) |

Values given in the parenthesis are taken from [9,10].

Table 3
Activation and reaction energies (kcal mol⁻¹) of the Cl₂CO+H₂O reaction in gas phase at B3LYP level with different basis sets

| Reaction | 6-31g (d) | | 6-31g (d,p) | | 6-311g (d) | | 6-31+g (d) | | 6-311++g (d,p) | |
|---|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | E _a | E _r | E _a | E _r | E _a | E _r | E _a | E _r | E _a | E _r |
| Cl ₂ CO+H ₂ O→Cl ₂ (OH) ₂ | 38.15 | -5.04 | 37.03 | -5.34 | 41.54 | -3.48 | 43.40 | -0.15 | 45.41 | 1.87 |
| Cl ₂ CO+H ₂ O→ClCOOH+HCl | 24.18 | -17.10 | 23.74 | -17.01 | 22.93 | -17.10 | 29.60 | -12.44 | 29.88 | -11.71 |
| Cl ₂ C(OH) ₂ →ClCOOH+HCl | 23.52 | -12.06 | 22.54 | -11.67 | 22.90 | -13.62 | 24.35 | -12.28 | 22.68 | -13.59 |
| ClCOOH→CO ₂ +HCl | 26.74 | -13.63 | 28.25 | -13.38 | 24.57 | -18.23 | 28.25 | -13.28 | 25.13 | -16.77 |

the direct formation of BrCOOH that is higher by 5.3 kcal mol⁻¹ than the formation of Br₂C(OH)₂ but the step Br₂C(OH)₂→BrCOOH+HBr is a high energy process. This renders Path 2 the mechanism of this reaction. In the present case, the difference in the activation energies for the formation of ClCOOH and Cl₂C(OH)₂ is found to be quite high, 15.54 kcal mol⁻¹ at B3LYP level (Table 1) and therefore the mechanism appears to be clearly resolved in favor of Path 2. The intermediate ClCOOH is more stabilized than the Cl₂C(OH)₂ and this is similar to the relative stability reported for BrCOOH and Br₂C(OH)₂. Between FCOOH and F₂C(OH)₂, the latter is reported to be more stable. Path 1 involves three steps and activation energies of these steps gradually decrease in the hydrolysis of F₂CO and Cl₂CO while in the hydrolysis of Br₂CO the second step, the decomposition of Br₂C(OH)₂ is found to be rate determining. The final step where the halo formic acid decomposes to give CO₂ and HX is found to be exothermic for Cl₂CO and Br₂CO while it is endothermic for F₂CO. Hydrolysis of F₂CO and Br₂CO in gas phase has been investigated by Zachariah et al. and Francisco, respectively, at different levels of theory and for comparison, activation energies of the most probable path (Path 2) of their reaction have been performed here and the values are listed in Table 2. The values obtained by Francisco and Zachariah et al. are given in parenthesis. From the values it is clear that the activation energies for both the transition states are highest for F₂CO reaction. Between Cl₂CO and Br₂CO, the former has smaller barrier for the first transition state and higher barrier for the second transition state compared to the latter.

3.3. Effect of basis set

In order to examine the effect of basis sets on the relative barrier heights, calculations have been performed with various basis sets at B3LYP level (Table 3); this level has been chosen because of the close agreement of the B3LYP results with the experimental values reported than any other ab initio method employed here. Moreover activation and reaction energies for the Br₂CO reactions at B3LYP/6-311++G (d,p) and QCISD/6-311++G(3df,2pd) level (Table 2) show close agreement and hence justifies the selection of B3LYP level for observing basis set effect. The data presented in Table 3 reveal that (i) addition of diffusion functions increased the activation barrier and decreased

the exothermicity; (ii) addition of p functions on hydrogen atoms has little effect on both. Activation energy trend in the three steps involved in Path 1 remained same on changing basis sets. But there is significant change in Path 2 when going from 6-31G(d) to 6-311++G (d, p); with lower basis sets the second step ClCOOH→CO₂+HCl is found to be rate determining but with higher basis sets Cl₂CO+H₂O→ClCOOH+HCl is found to be rate determining. The latter trend is acceptable and in close agreement with the trend reported for F₂CO and Br₂CO hydrolysis.

3.4. Geometry and structure

Structures of TS1–TS4 are presented in Fig. 2. All are four-membered cyclic transition states. TS1 describes the addition of H₂O across C=O bond. The C=O bond and one of the two O–H bonds in H₂O break and new C–O and O–H bonds form. TS2 explains addition of H₂O across C–Cl bond of Cl₂CO and simultaneous elimination of HCl. C–Cl and O–H bonds lengthen and C–O and HCl bonds form. The bond lengths values of TS1 and TS2 indicate that in TS2 formation of C–O and cleavage of O–H are lower in degree compared to TS1. Therefore, TS2 must be loose compared to TS1 and this explains relatively lower barrier for Path 2. TS3 shows the elimination of HCl from Cl₂C(OH)₂. In this C=O bond is partially restored and HCl bond forms, C–Cl and O–H bonds break. TS4 describe the elimination of HCl from ClCOOH. The formation of second carbonyl bond and H–Cl bond is clearly visible from the bonds noted in Fig. 2. In TS4 C–Cl and O–H bonds are broken partially.

3.5. Effect of second water molecule on the reaction path

The influence of second water molecule on several hydrolytic reactions has already been reported [7,17–20] and in a similar way the effect of second water molecule on the hydrolysis of Cl₂CO with water has been studied here. Specifically, the second water molecule is added to the species on the kinetically favored Path 2 and computations have been done at B3LYP/6-311++G (d, p) level. There are three possibilities of adding the second water molecule to the reacting system; that is the reacting system can be considered as Cl₂CO+2H₂O or Cl₂CO⋯H₂O+H₂O or Cl₂CO+(H₂O)₂ and in this the first one is less probable as it involves intermolecular collision. In the latter two, the third one is energetically more stable than the second and

therefore Cl_2CO and water dimer $(\text{H}_2\text{O})_2$ is considered as the reactant. This forms the weak complex WC2 in the first step (Scheme 2). Optimized geometries of the species on the reaction surface are presented in Fig. 3 and their potential energy surface is given in Fig. 1(b). In this complex, the distance between the carbonyl carbon and the oxygen of the first water molecule is found to be 2.95 Å and the second water molecule is hydrogen bonded to both oxygen of the carbonyl dichloride and the first water molecule. Inclusion of second water molecule on the reaction path stabilizes the weak complex by 4.6 kcal mol⁻¹ with respect to the reactants. The next step of the reaction is the formation of transition state TS5. This transition state is stabilized by the second water molecule and the barrier height is 24.6 kcal mol⁻¹ with respect to the reactant and 29.1 kcal mol⁻¹ with respect to the weak complex. The barrier height with respect to the reactant for the step 2 is about 5.3 kcal mol⁻¹ less than that of the reaction with one water molecule. TS5 eliminates one molecule of HCl and forms the intermediate $\text{ClCOOH}\cdots\text{H}_2\text{O}$ and is denoted as weak complex 3 (WC3) in Fig. 3. This intermediate is stabilized by 15.9 kcal mol⁻¹ with respect to the reactant. Following this, this complex will eliminate one molecule of HCl again by an intermolecular process, elimination of HCl by Cl from ClCOOH moiety and H from hydrogen bonded H_2O moiety or less probably through an intramolecular hydrogen bonding and finally form CO_2 and HCl. Addition of one water molecule decreases the relative energy of weak complex (WC2 and WC3) of the transition state (TS5) by 4–5 kcal mol⁻¹ compared to that of a single water molecule. This decrease in energy is clearly due to the possible hydrogen bonding found between the water molecules.

4. Conclusions

Carbonyl dichloride undergoes hydrolysis to form finally CO_2 and HCl and computations show that a weak complex is initially formed and following this there are two paths opened for this reaction. Water can either add across the carbonyl bond to form dichloromethane diol (Path 1) or across C–Cl bond to form chloro formic acid directly (Path 2). The diol decomposes to give chloro formic acid subsequently. Finally, chloro formic acid eliminates one molecule of HCl to give CO_2 . Path 2 that describes direct formation of chloro formic acid is found to be low lying and is kinetically favorable. Between ab initio and DFT methods, ab initio method overestimates the barriers with reference to experimental results. While addition of diffuse functions recovers more correlation energy, addition of

polarization function on hydrogen atoms does not alter the energies significantly. The influence of second water molecule on the reaction has been studied and this shows that the second water molecule is found to catalyze the reaction by drastically reducing the barrier from 29.9 to 24.6 kcal mol⁻¹. Hydrolysis of Cl_2CO was performed at high temperatures and the activation energy was calculated to be 14.2 ± 2.1 kcal mol⁻¹ from the experimental data points that showed large scatter. Hydrolysis of Cl_2CO follows the same mechanism that both F_2CO and Br_2CO undergo in gas phase. Activation and reaction energies computed for the hydrolysis of Br_2CO at B3LYP/6-311 + +G(d,p) level are in close agreement with the values reported [10] at QCISD/6-311 + +G(3df,2pd) level.

Acknowledgements

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